

Effect of linear temperature dependence of thermoelectric properties on energy conversion efficiency

Osamu Yamashita *

Materials Science Company Limited, 5-5-44, Minamikasugaoka, Ibaraki, Osaka 567-0046, Japan

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ABSTRACT

New thermal rate equations were developed by taking the temperature dependences of the electrical resistivity ρ and thermal conductivity κ of the thermoelectric (TE) materials into the thermal rate equations on the assumption that they vary linearly with temperature T . The relative energy conversion efficiency η/η_0 for a single TE element was formulated by approximate analysis, where η and η_0 are the energy conversion efficiencies derived from the new and conventional thermal rate equations, respectively. Applying it to Si–Ge alloys, the temperature dependence of ρ is stronger than that of κ , so the former has a more significant effect on η/η_0 than the latter. However, the degree of contribution from both of them to η/η_0 was a little lower than 1% at the temperature difference ΔT of 600 K. When the temperature dependence of κ was increased to become equal to that of ρ , however, it was found that η/η_0 is increased by about 10% at $\Delta T = 600$ K. It is clarified here that the temperature dependences of ρ and κ are also important factors for an improvement in η .

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1. Introduction

There has been considerable interest during the past ten years in finding new materials and structures for use in clear, highly efficient cooling and energy conversion systems [1,2]. The thermoelectric (TE) figure of merit ZT provides a measure of the quality of such materials for applications and is defined by $ZT = \alpha^2 T / \rho \kappa$, where α is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity and T is the absolute temperature [1]. The increase in ZT leads directly to improvement in the energy conversion efficiency of TE generators and in the cooling efficiency of Peltier modules [3]. Much effort has been made to raise the ZT of TE bulk materials for energy conversion efficiency, so there have been some improvements in ZT (for example, ~ 2 at 700 K for the p-type TAGS (GeTe-AgSbTe_2) [4], about 1.4 at 620 K for the p-type $\text{CeFe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$ skutterudite compound [5] and about 1.5 at 700 K for the p-type (Zr–Hf)NiSn half-Heusler compound [6]). However, even their values are not sufficient to improve dramatically the energy conversion efficiency (η).

The energy conversion efficiency η has been calculated analytically using the well known thermal rate equations at the cold and hot junctions of a TE element [3]. The change in α with temperature has been taken into the conventional thermal rate equations. However, the variations in ρ and κ with temperature were neglected, although generally they have different values at the hot

and cold junctions [7]. The traditional expressions for η obtained from the conventional thermal rate equations should, thus, not be exactly correct. For this reason, η has been calculated numerically by solving the differential equations governing TE properties by the software tool in which the correct temperature dependence of TE properties is taken into account [8]. However, such a calculation has never clarified analytically the degree to which the temperature dependence of each TE property has an effect on η . To make it clear, we made an attempt to take the difference between the TE properties at the hot and cold sides of a TE element into the thermal rate equations on the assumption that all of the TE properties change linearly with temperature. The new thermal rate equations were, thus, formulated by taking the new temperature dependences of both ρ and κ into the thermal rate equations. The reason that only the linear temperature dependence of TE properties was employed here is simply to make clear the effect of the temperature dependence of TE properties on η . It is clarified for Si–Ge alloys [9] in this paper how η/η_0 varies with changes in the sign and magnitude in the gradients of ρ and κ for T , where η/η_0 is the relative energy conversion efficiency calculated using the new and conventional thermal rate equations, respectively. The reason that Si–Ge alloys were employed for the calculation of η/η_0 is that their TE properties indeed change linearly with temperature in the broad temperature region from 400 to 1000 K. η was then derived analytically on the assumption that the terms dependent on the temperature difference ΔT imposed on a TE element are sufficiently small compared with those independent of ΔT .

* Tel./fax: +81 72 626 6585.

E-mail address: yamashio567@yahoo.co.jp

Nomenclature

TE	thermoelectric	D	normalized temperature dependence of $Z(T)$ at T (defined as $D = (dZ(T)/dT)/Z(T)$ (K^{-1}))
Z	thermoelectric figure of merit (K^{-1})	Q_h	heat energy at hot junction of TE element (W)
ZT	dimensionless thermoelectric figure of merit	Q_c	heat energy at cold junction of TE element (W)
T	mean temperature of TE element (given by $T = (T_h + T_c)/2$) (K)	Q	difference ($Q_h - Q_c$) in heat energy between both end junctions of TE element (W)
ΔT	temperature difference between both ends of TE element (K)	S	cross sectional area of TE element (m^2)
T_z	temperature at position z of TE element (K)	L	length of thermoelectric material of TE element (m)
T_h	temperature at hot junction of TE element (given by $T + \Delta T/2$) (K)	R_L	load resistance (Ω)
T_c	temperature at cold junction of TE element (given by $T - \Delta T/2$) (K)	I	electric current through TE element (A)
$K(T)$	thermal conductance given by $K(T) = S\kappa(T)/L$ (W/K)	Greek letters	
$R(T)$	electric resistance given by $R(T) = L\rho(T)/S$ (Ω)	α	Seebeck coefficient of material (V/K)
$\langle K(T_h) \rangle$	thermal conductance averaged over half (hot) side of TE element (W/K)	$\alpha(T_h)$	Seebeck coefficient at hot junction of TE element (V/K)
$\langle K(T_c) \rangle$	thermal conductance averaged over half (cold) side of TE element (W/K)	$\alpha(T_c)$	Seebeck coefficient at cold junction of TE element (V/K)
$\langle R(T_h) \rangle$	electrical resistivity averaged over half (hot) side of TE element (Ω)	κ	thermal conductivity of material (W/mK)
$\langle R(T_c) \rangle$	electrical resistivity averaged over half (cold) side of TE element (Ω)	ρ	electrical resistivity of material (Ω m)
A	normalized temperature dependence of $\alpha(T)$ at T (defined as $A = (d\alpha(T)/dT)/\alpha(T)$ (K^{-1}))	γ	parameter defined as $(1 + ZT) - 1/2$
B	normalized temperature dependence of $\rho(T)$ at T (defined as $B = (d\rho(T)/dT)/\rho(T)$ (K^{-1}))	$\beta(T_h)$	Thomson coefficient at hot junction of TE element (defined as $T_h(d\alpha/dT)$) (V/K)
C	normalized temperature dependence of $\kappa(T)$ at T (defined as $C = (d\kappa(T)/dT)/\kappa(T)$ (K^{-1}))	$\beta(T_c)$	Thomson coefficient at cold junction of TE element (defined as $T_c(d\alpha/dT)$) (V/K)
		η	energy conversion efficiency for $B \neq 0$ K^{-1} and $C \neq 0$ K^{-1} (%)
		η_0	energy conversion efficiency for $B = C = 0$ K^{-1} (%)

The purpose of this paper is to investigate to what extent the temperature dependences of ρ and κ of TE materials have an effect on η of a single TE element and to show whether η/η_0 of a TE element can be enhanced significantly by improving the temperature dependences of ρ and κ .

2. Analysis

2.1. Temperature dependence of thermoelectric properties

Let us consider a single TE element in which a TE parallelepiped is welded with two electrically conducting materials, as shown in Fig. 1. When a temperature difference is imposed on a TE element, a voltage is generated between both ends of a TE element, and a current flows through a circuit. The current can then be used to

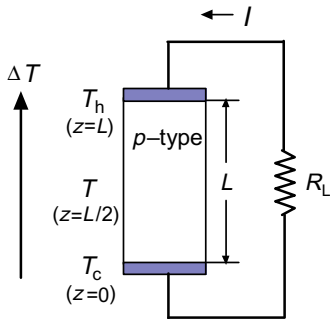


Fig. 1. A single TE element (possessing the length L and cross-sectional area S) sandwiched between two metals on which the temperature difference ΔT is imposed, where T_h and T_c are the temperatures at the hot and cold junctions, T is the mean element temperature and I is a current flowing through a circuit composed of a TE element and a load resistance R_L .

power a load, thus converting the thermal energy into electric energy. For a majority of cases, a one dimensional model has been sufficient to obtain quantitatively correct performance data [10]. Assuming that the temperature difference between the hot (T_h) and cold (T_c) junctions of a TE element is ΔT and the mean temperature is T , T_h and T_c are expressed as $T + \Delta T/2$ and $T - \Delta T/2$, respectively. Thus, the energy conversion efficiency η should depend strongly on the temperature dependence of the TE properties of TE materials because the TE properties are different at the hot and cold junctions.

Here, let us assume that the Seebeck coefficient $\alpha(T)$, the electric resistance $R(T)$ and the thermal conductance $K(T)$ of a TE element change linearly with an increase of T over a working temperature range, where T is the mean temperature. $\alpha(T_h)$ at the hot junction and $\alpha(T_c)$ at the cold junction of a TE element are then expressed as a function of ΔT as

$$\alpha(T \pm \Delta T/2) = \alpha(T)(1 \pm A\Delta T/2), \quad (1)$$

and $R(T_h)$ and $K(T_h)$ at the hot side and $R(T_c)$ and $K(T_c)$ at the cold side of a TE element are given in the same way by

$$R(T \pm \Delta T/2) = R(T)(1 \pm B\Delta T/2) \quad (2)$$

and

$$K(T \pm \Delta T/2) = K(T)(1 \pm C\Delta T/2), \quad (3)$$

where $A = (d\alpha(T)/dT)/\alpha(T)$, $B = (dR(T)/dT)/R(T)$ and $C = (dK(T)/dT)/K(T)$. The difference in α between both junctions has been taken into the conventional thermal rate equations, but the differences in R and K between the hot and cold sides have always been neglected. In the conventional thermal rate equation, α has been replaced with an average value $\langle \alpha \rangle$ over a working temperature range, and the resistances of the hot and cold sides were replaced by $R/2$ so that the Joule heat is divided equally between the hot and cold sides. As for K , the K value at the mean temperature has hitherto been em-

ployed for the thermal rate equations, so that $K(T)$ was regarded as a constant throughout a TE element. Thus, the temperature dependence of $R(T)$ and $K(T)$ has never been taken into account in the conventional thermal rate equations.

When $\rho(T)$ and $\kappa(T)$ change linearly with T , it is shown that if we divide $R(T)$ of a TE element into $\langle R(T_h) \rangle$ and $\langle R(T_c) \rangle$ averaged over a half (hot or cold) side of a TE element and replace $K(T)$ with $\langle K(T) \rangle$ averaged all over a TE element, they can be expressed using the average gradients in ρ and κ for T . The reason that the resultant $\langle K(T) \rangle$ was employed here for the thermal rate equations instead of $\langle K(T_h) \rangle$ and $\langle K(T_c) \rangle$ is that the thermal conductance must be considered as a total thermal conductance. As described in the Appendix, when the temperature within a TE parallelepiped changes linearly along its length direction (see Fig. 1), the average $\langle R(T_h) \rangle$ and $\langle R(T_c) \rangle$ of the hot and cold sides are then expressed as

$$\langle R(T_h) \rangle = (R(T)/2)(1 + B\Delta T/4) \quad (4)$$

and

$$\langle R(T_c) \rangle = (R(T)/2)(1 - B\Delta T/4) \quad (5)$$

as a function of ΔT . However, the sum of $\langle R(T_h) \rangle$ and $\langle R(T_c) \rangle$ is equal to $R(T)$. The conventional theory has taken $B = 0 \text{ K}^{-1}$, but we will take here $B \neq 0 \text{ K}^{-1}$ because $B\Delta T/4$ has a value of 0.19 on average at $\Delta T = 600 \text{ K}$ in Si-Ge alloys [8], a value that is not negligibly small compared with 1.

When ΔT is applied to a TE element, the resultant $\langle K(T) \rangle$ averaged all over a TE element is expressed as

$$\langle K(T) \rangle = K(T)[1 - (C\Delta T)^2/12], \quad (6)$$

as described in the Appendix, if $(C\Delta T)^2/12$ is very small compared with 1, where $K(T) = S\kappa(T)/L$. The resultant $\langle K(T) \rangle$ depends on the term of C^2 , not on C . It is, thus, found that the resultant $\langle K(T) \rangle$ tends to decrease significantly with an increase of ΔT , irrespective of the sign of C .

2.2. η derived by taking into account the temperature dependence of thermoelectric properties

Here, we make an attempt to take the temperature dependences of TE properties into the energy conversion efficiency η . First of all, we derive the new thermal rate equations using $\alpha(T_h)$, $\alpha(T_c)$, $\langle R(T_h) \rangle$, $\langle R(T_c) \rangle$, $\beta(T_h)$ and $\beta(T_c)$, where $\beta(T_h)$ and $\beta(T_c)$ are the Thomson coefficients given by the relations $\beta(T_h) = T_h(d\alpha/dT)$ and $\beta(T_c) = T_c(d\alpha/dT)$ [11]. When ΔT is applied to a TE element and the Seebeck and Thomson effects result in power generation, the thermal rate equations for a TE element can be expressed as

$$Q_h = [\alpha(T_h) - \beta(T_h)\Delta T/2T_h]I - \langle R(T_h) \rangle I^2 + \langle K(T) \rangle \Delta T \quad (7)$$

and

$$Q_c = [\alpha(T_c) + \beta(T_c)\Delta T/2T_c]I + \langle R(T_c) \rangle I^2 + \langle K(T) \rangle \Delta T, \quad (8)$$

where T is the mean TE element temperature of $(T_h + T_c)/2$, $\langle K(T) \rangle$ is the resultant average thermal conductance under ΔT , and Q_h and Q_c are the thermal energies heated and cooled at the hot and cold junctions, respectively [12]. The first, second and third terms in both equations represent the Peltier and Thomson effects, Joule heating and thermal conduction, respectively. When $\langle R(T_h) \rangle = \langle R(T_c) \rangle = R(T)/2$ and $\langle K(T) \rangle = K(T)$, these equations correspond to the thermal equations reported by Min et al. [12]. Using the relation between the Thomson coefficient β and A defined in the previous subsection, the following relations are obtained as

$$\beta(T_h) = T_h A \alpha(T) \quad (9)$$

and

$$\beta(T_c) = T_c A \alpha(T). \quad (10)$$

By substituting Eqs. (1), (4), (5), (9) and (10) into Eqs. (7) and (8), the new thermal rate equations are expressed as

$$Q_h = \alpha(T)T_h I - R(T)(1 + B\Delta T/4)I^2/2 + K(T)[1 - (C\Delta T)^2/12]\Delta T \quad (11)$$

and

$$Q_c = \alpha(T)T_c I + R(T)(1 - B\Delta T/4)I^2/2 + K(T)[1 - (C\Delta T)^2/12]\Delta T, \quad (12)$$

at least when there is no heat transfer to or from the surroundings other than a TE element. After all, the term A is canceled by that of the Thomson coefficient, as already pointed out by Ioffe [7], so that only the terms B and C^2 remain in the thermal rate equations. If $B = C = 0 \text{ K}^{-1}$, of course, these thermal rate equations reduce to the conventional thermal rate equations [7]. The energy difference Q between Q_h and Q_c is given by

$$Q = Q_h - Q_c = \alpha(T)\Delta T I - R(T)I^2 = R_L I^2, \quad (13)$$

where $R_L I^2$ is the electric energy consumed in a load resistance R_L [7]. From Eq. (13), the current I flowing through a circuit is obtained simply as

$$I = \frac{\alpha(T)\Delta T}{(R_L + R(T))} \quad (14)$$

The energy conversion efficiency η of a TE element is defined as Q/Q_h [7] and is expressed as

$$\begin{aligned} \eta &= Q/Q_h \\ &= \frac{R_L I^2}{\alpha(T)T_h I - R(T)(1 + B\Delta T/4)I^2/2 + K(T)[1 - (C\Delta T)^2/12]\Delta T} \end{aligned} \quad (15)$$

By substituting Eq. (14) into Eq. (15) and setting $R_L/R(T) = m$, η is rewritten as

$$\begin{aligned} \eta &= Q/Q_h \\ &= \frac{Z\Delta T m}{(1 + m)^2[1 - (C\Delta T)^2/12] + ZT_h(1 + m) - (1 + B\Delta T/4)(Z\Delta T)/2}, \end{aligned} \quad (16)$$

where $Z = \alpha(T)^2/R(T)K(T)$. By making $d\eta/dm$ equal to zero, the quadratic equation of m for maximum η is obtained as

$$(1 - m^2)[1 - (C\Delta T)^2/12] + ZT_h - (1 - B\Delta T/4)(Z\Delta T)/2 = 0. \quad (17)$$

When the values of $(C\Delta T)^2/12$ and $B\Delta T/4$ are very small compared with 1, Eq. (17) is rewritten as

$$m^2 = \gamma^{-2}[1 + (1 - \gamma^2)(\Delta T)^2(2TC^2 - 3B)/24T] \quad (18)$$

and

$$m = \gamma^{-1}[1 + (1 - \gamma^2)(\Delta T)^2(2TC^2 - 3B)/48T], \quad (19)$$

where

$$\gamma = (1 + ZT)^{-1/2}. \quad (20)$$

By substituting Eqs. (18) and (19) into Eq. (16), moreover, the energy conversion efficiency η is expressed by a similar approximation as

$$\eta = \eta_0 \left\{ 1 + \frac{(\Delta T)^2 \gamma}{4(\gamma T_c + T_h)} \left[\frac{B(1 - \gamma)}{2} + \frac{C^2 T(1 + \gamma)}{3} \right] \right\}, \quad (21)$$

where η_0 is the original energy conversion efficiency derived from the conventional thermal rate equations and is expressed as [7]

$$\eta_0 = \frac{(1 - \gamma)\Delta T}{(\gamma T_c + T_h)} \quad (22)$$

Although Eq. (21) is derived by an approximate analysis, it is sufficient to investigate the effect of B and C on η . It is, thus, found that when α , R and K have a linear dependence on temperature, only the terms related to the temperature dependences of R and K remain in η . Of course, η is reduced to η_0 for $B = C = 0 \text{ K}^{-1}$. Since the coefficients of B and C^2 are always positive in sign because of $\gamma < 1$, the increase in B and C^2 , thus, results directly in an increase in η/η_0 . However, the ideal Carnot efficiency of η is obtained in the limit as $ZT \rightarrow \infty$ ($\gamma \rightarrow 0$), as in the case of η_0 , irrespective of the presence of B and C .

The thermoelectric figures of merit Z at T_h and T_c were calculated using Eqs. (1)–(3). When the products of A , B and C and ΔT are very small compared with 1, the expressions for $Z(T_h)$ and $Z(T_c)$ at the hot and cold junctions are expressed approximately as

$$Z(T_h) = [\alpha(T_h)^2 / R(T_h)K(T_h)] = Z(T)[1 + (2A - B - C)\Delta T/2] \\ = Z(T)(1 + D\Delta T/2) \quad (23)$$

and

$$Z(T_c) = [\alpha(T_c)^2 / R(T_c)K(T_c)] = Z(T)[1 - (2A - B - C)\Delta T/2] \\ = Z(T)(1 - D\Delta T/2), \quad (24)$$

using A , B and C and ΔT , where $Z(T) = \alpha(T)^2 / R(T)K(T)$ and $D = 2A - B - C$. $Z(T_h)$ and $Z(T_c)$ are, thus, found to change significantly with ΔT according to the value of D . When $D = 0 \text{ K}^{-1}$, of course, Z never varies with changes in T . The gradient of Z for T is obtained from the relation $dZ/dT = [Z(T_h) - Z(T_c)]/\Delta T$ as

$$dZ/dT = ZD \quad (25)$$

using Eqs. (23) and (24).

3. Results and discussions

3.1. Parameters of A , B , C , D and β obtained for the p- and n-type Si-Ge alloys

Figs. 2 and 3 show the temperature dependences of α , ρ , κ and Z measured for the p-type $\text{Si}_{0.95}\text{Ge}_{0.05}$ alloy doped with B and n-type $\text{Si}_{0.95}\text{Ge}_{0.06}$ alloy doped with P, which have values of $ZT = 0.57$ and 0.90 at 1073 K , respectively [9]. The TE properties of Si-Ge alloys change almost linearly with temperature, as shown in Figs. 2 and 3. For this reason, the parameters of A , B , C and D were calculated using Eqs. (1), (2), (3) and (25) from the experimental values of α , ρ , κ and Z for Si-Ge alloys in the temperature range from 400 to 1000 K , as listed in Table 1. There was no significant difference in A , B , C and D between the p- and n-type Si-Ge alloys. In both the p- and n-type Si-Ge alloys, A , B and D are positive in sign, but C is negative in sign. Of course, the values of A , B , C and D change somewhat with the chemical composition of Si-Ge alloys [13,14] or its fabrication method. The present D values obtained from the temperature dependence of Z agree with the resultant values of $(2A - B - C)$ (see Table 1) within 4%. It indicates that the present approximation is valid for Si-Ge alloys.

The Thomson coefficients β for the p- and n-type Si-Ge alloys were calculated using Eqs. (9) and (10). As a result, $\beta(T_h)$ at $T_h = 1000 \text{ K}$ was $175 \text{ } \mu\text{V/K}$ for the p-type alloy and $-237 \text{ } \mu\text{V/K}$ for the n-type one. In contrast, $\beta(T_c)$ at $T_c = 400 \text{ K}$ was $70 \text{ } \mu\text{V/K}$ for the p-type alloy and $-95 \text{ } \mu\text{V/K}$ for the n-type one. The values of $\beta(T_h)$ were much higher in absolute value than the $\beta = 129 \text{ } \mu\text{V/K}$ estimated theoretically by Ioffe [7] using a non-degenerate model, while those of $\beta(T_c)$ were much lower in absolute value than $\beta = 129 \text{ } \mu\text{V/K}$. The band structure of Si-Ge alloys might, thus, change from a degenerate state to a non-degenerate one with an increase of temperature.

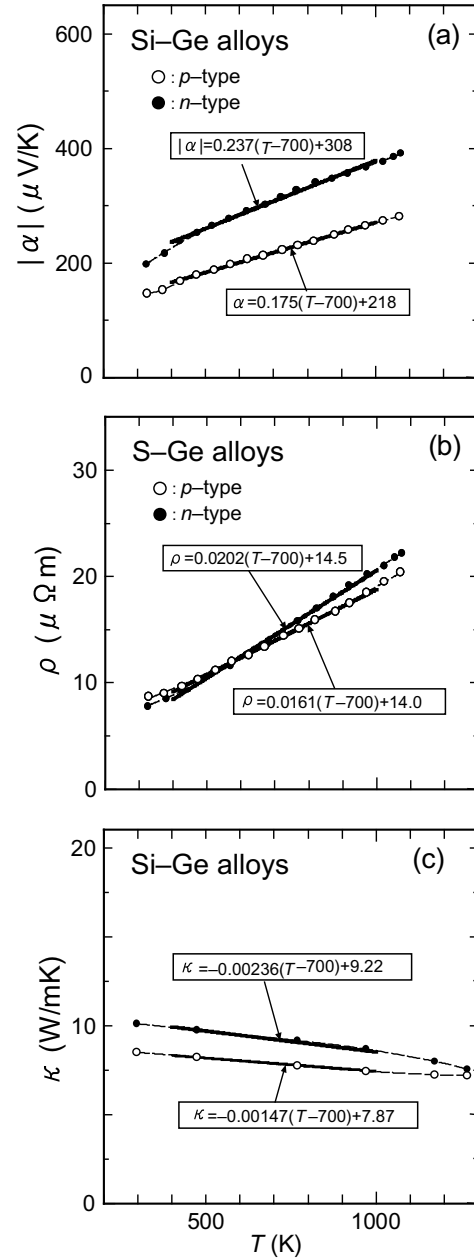


Fig. 2. Temperature dependences of (a) $|\alpha|$, (b) ρ and (c) κ measured by us for the p- and n-type Si-Ge alloys (Ref. [9]).

3.2. Dependence of η/η_0 on ΔT , B and C

The dependence of η/η_0 on ΔT was calculated using Eq. (21) as a function of ΔT using $B = 1.15 \times 10^{-3} \text{ K}^{-1}$ and $C = -1.87 \times 10^{-4} \text{ K}^{-1}$ for the p-type Si-Ge alloy and $B = 1.39 \times 10^{-3} \text{ K}^{-1}$ and $C = -2.56 \times 10^{-4} \text{ K}^{-1}$ for the n-type [9] (see Table 1), as shown in Fig. 4. Consequently, η/η_0 of the p- and n-type alloys increase parabolically with an increase of ΔT and increased to 1.005 for the p-type alloy and to about 1.009 at $\Delta T = 600 \text{ K}$. As shown in the figure, the degree of contribution from the term of B to η/η_0 is about 4.6 times larger than that from the term of C . The degree of increase in η/η_0 due to the contribution of B and C is a little lower than 1% at $\Delta T = 600 \text{ K}$ for the present Si-Ge alloys. If the values of their parameters remain unvaried with ΔT , however, η/η_0 would be enhanced significantly with further increase in ΔT .

Next, the dependence of η/η_0 on B and C was calculated as a function of $X(=B = |C|)$ at the mean temperature of $T = 700 \text{ K}$ using

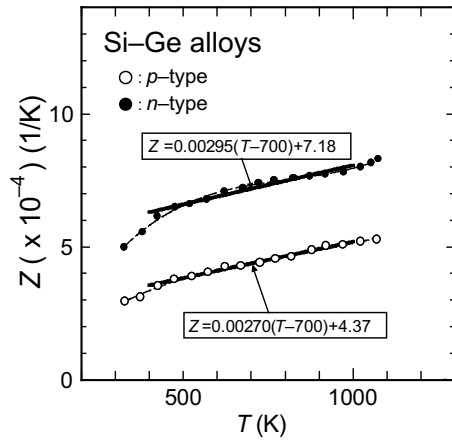


Fig. 3. Temperature dependences of Z measured for the p- and n-type Si-Ge alloys (Ref. [9]).

Table 1

The values of A , B , C and D at $T = 700$ K estimated from the temperature dependences of the thermoelectric properties measured for the p- and n-type Si-Ge alloys (Ref. [9])

Items (K^{-1})	p-type	n-type
A	8.03×10^{-4}	7.69×10^{-4}
B	1.15×10^{-3}	1.39×10^{-3}
C	-1.87×10^{-4}	-2.56×10^{-4}
$2A-B-C$	6.43×10^{-4}	4.04×10^{-4}
D	6.18×10^{-4}	4.11×10^{-4}

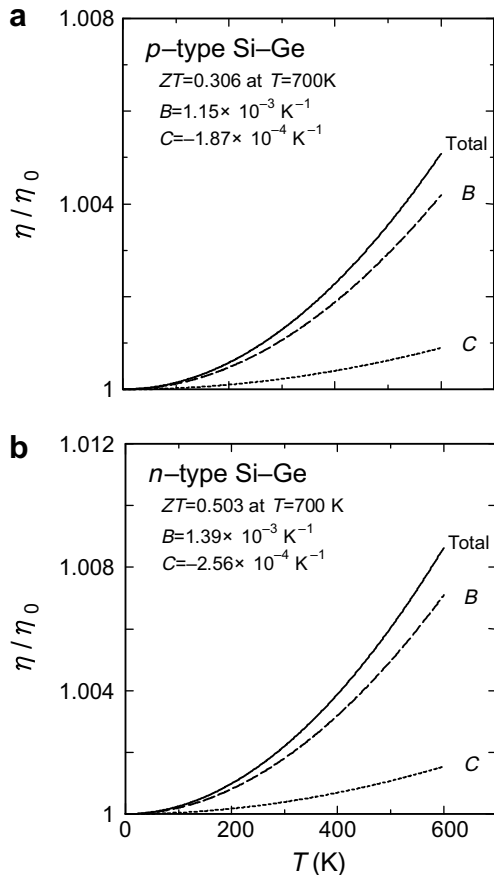


Fig. 4. η/η_0 calculated as a function of ΔT at $T = 700$ K for the p- and n-type Si-Ge alloys (Ref. [9]) using their analytical values of B and C .

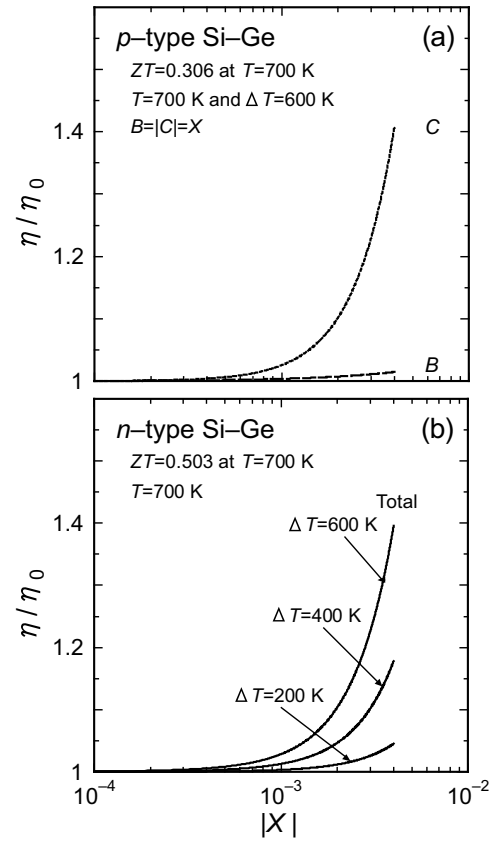


Fig. 5. η/η_0 calculated at $T = 700$ K as a function of X under various temperature conditions of (a) $\Delta T = 600$ K for the p-type Si-Ge alloy and of (b) $\Delta T = 200, 400$ and 600 K for the n-type Si-Ge alloy, where $X = B = |C|$.

Eq. (21) under the conditions of $\Delta T = 600$ K for the p-type Si-Ge alloy and of $\Delta T = 200, 400$ and 600 K for the n-type one and plotted as a function of X in Fig. 5. η/η_0 tends to increase linearly with an increase of B but parabolically with an increase of $|C|$, so that the degree of contribution from C to η/η_0 is 14 times larger than that from B at $X = 2 \times 10^{-3} K^{-1}$. Using η/η_0 derived approximately from the thermal rate equations, one estimates the degrees of contribution from B and C to η/η_0 . However, the present results would be almost unvaried fundamentally even if one employed η/η_0 derived exactly from them. With our Si-Ge alloys, the values of B are relatively close to $2 \times 10^{-3} K^{-1}$, while those of $|C|$ are only about a tenth of $2 \times 10^{-3} K^{-1}$. Even at $C = 2 \times 10^{-3} K^{-1}$, the present approximation is valid because $(C\Delta T)^2/12$ in Eq. (6) is 0.12 at $\Delta T = 600$ K, which is fully small compared with 1. Indeed, there is a TE material having a $|C|$ value close to $2 \times 10^{-3} K^{-1}$ among the TE materials for energy conversion; for example, $|C| = 1.8 \times 10^{-3} K^{-1}$ for $CoSb_3$ [15]. Therefore, the value assumed here for C is not imaginary but realistic. Interestingly, as is evident from Eq. (21), η/η_0 of a TE element is enhanced significantly even when $D = 0 K^{-1}$ (for example, $A = 0 K^{-1}$ and $B = -C = 2 \times 10^{-3} K^{-1}$). Moreover, when B and $|C|$ have a large value of $2 \times 10^{-3} K^{-1}$, η/η_0 is found to be enhanced by about 10% at $\Delta T = 600$ K, as shown in Fig. 5. In any case, the sign and magnitude of B and the magnitude of C are found to be very important to enhance η as high as possible.

3.3. $Z_{eff}T$ obtained by ascribing the increase in η/η_0 due to B and C to the increase in the intrinsic ZT

The effective $Z_{eff}T$ for a TE element was calculated by ascribing the increase in η/η_0 due to B and C to the increase in the intrinsic ZT . For simplicity, Eq. (21) is rewritten as

$$\frac{\eta}{\eta_0} = 1 + Y \quad (26)$$

where

$$Y = \frac{(\Delta T)^2 \gamma}{4(\gamma T_c + T_h)} \left[\frac{B(1 - \gamma)}{2} + \frac{C^2 T(1 + \gamma)}{3} \right], \quad (27)$$

where $\gamma = (1 + ZT)^{-1/2}$. If we attribute the increase in η/η_0 due to B and C to the increase in the intrinsic ZT , η is expressed as

$$\eta = \frac{(1 - \gamma_{\text{eff}}) \Delta T}{(\gamma_{\text{eff}} T_c + T_h)} \quad (28)$$

using the effective $\gamma_{\text{eff}} = (1 + Z_{\text{eff}} T)^{-1/2}$. Substituting Eqs. (22) and (28) into Eq. (26), the following equation is obtained as

$$\gamma_{\text{eff}} = \gamma - \frac{(1 - \gamma)(\gamma T_c + T_h) Y}{2T} \quad (29)$$

Substituting Eq. (27) into Eq. (29), moreover, the effective $Z_{\text{eff}} T$ is expressed by a similar approximation as

$$Z_{\text{eff}} T = ZT \left[1 + \frac{(\Delta T)^2}{4T} \left(\frac{B(1 - \gamma)}{2(1 + \gamma)} + \frac{C^2 T}{3} \right) \right] \quad (30)$$

using ZT , B and C . This expression shows that $Z_{\text{eff}} T$ is always larger than the intrinsic ZT if $B > 0$. It indicates that the presence of B and C results in a substantial increase in ZT if $B > 0$. In order to investigate the effect of the increase in η/η_0 due to B and C on $Z_{\text{eff}} T$, $Z_{\text{eff}} T$ and $ZT/Z_{\text{eff}} T$ were calculated as a function of ZT at $T = 700$ K using Eq. (30) under the temperature differences of $\Delta T = 200, 400$

and 600 K for $X = B = |C| = 2 \times 10^{-3} \text{ K}^{-1}$. The effective $Z_{\text{eff}} T$ is well defined even at $\Delta T = 600$ K, because the present approximation holds even for $\Delta T = 600$ K and $X = 2 \times 10^{-3} \text{ K}^{-1}$, as mentioned earlier. As shown in Fig. 6a, $Z_{\text{eff}} T$ increases almost linearly with an increase of ZT and the gradient of $Z_{\text{eff}} T$ for ZT tends to be enhanced more strongly at larger ΔT . The ratio of $(Z_{\text{eff}} T)/(ZT)$ also increases more significantly with an increase of the intrinsic ZT at larger ΔT , as shown in Fig. 6b. It suggests that the effective $Z_{\text{eff}} T$ of a TE element is enhanced significantly even when $D = 0 \text{ K}^{-1}$ (for example, $A = 0 \text{ K}^{-1}$ and $B = -C = 2 \times 10^{-3} \text{ K}^{-1}$). It was, thus, found that the sign and magnitude of the temperature dependences of TE properties have a significant influence on the energy conversion efficiency η of a TE element, particularly at large ΔT .

4. Conclusions

The new thermal rate equations were constructed by introducing newly the temperature dependences of ρ and κ of TE materials on the assumption that they vary linearly with temperature. The term of linear temperature dependence of α disappears but those of ρ and κ remain in the thermal rate equations. The energy conversion efficiency η for a single TE element was first formulated by approximate analysis, so that the formula derived here for η can be utilized for estimation of a TE element in which each TE property has a linear temperature dependence. η/η_0 was derived and calculated as functions of ΔT , ZT , B and C for Si-Ge alloys, where $B = (d\rho/dT)/\rho$ and $C = (d\kappa/dT)/\kappa$, so that η/η_0 was found to be enhanced significantly by the value of B rather than C with an increase of ΔT . When C becomes equal to B in absolute magnitude, however, the major part of the increase in η/η_0 results from $|C|$ and η/η_0 is increased by approximately 10% at $\Delta T = 600$ K. When we ascribed this increase in η/η_0 due to B and C to the increase in ZT , it is found that the degree of increase in ZT at $\Delta T = 600$ K corresponds to approximately 10% at $X = B = |C| = 2 \times 10^{-3} \text{ K}^{-1}$. The approximate expression obtained here for η reflects sufficiently the effect of the temperature dependence of ρ and κ on η . It was clarified by taking the temperature dependences of ρ and κ into the thermal rate equations so that they also contribute to an enhancement of the energy conversion efficiency η .

Appendix A

Let us assume that the Seebeck coefficient α , the electric resistance R and the thermal conduction K of a TE parallelepiped increase or decrease linearly with an increase of T . Here, we will show that $\langle R(T_h) \rangle$ or $\langle R(T_c) \rangle$ averaged over a half (hot or cold) side of a TE element and the resultant $\langle K(T) \rangle$ averaged all over an element are expressed as a function of ΔT . When we assume that the temperature in a TE parallelepiped changes linearly with z along its length direction, as shown in Fig. 1, the temperature T_z at a position z is expressed as

$$T_z = T + (z - L/2) \Delta T / L. \quad (\text{A.1})$$

When the electrical resistivity ρ changes linearly with T , $\rho(T_z)$ at T_z is then expressed as

$$\rho(T_z) = \rho(T) [1 + (T_z - T) B], \quad (\text{A.2})$$

where

$$B = \frac{1}{\rho(T)} \frac{d\rho(T_z)}{dT_z} = \frac{1}{R(T)} \frac{dR(T_z)}{dT_z} \quad (\text{A.3})$$

Therefore, the average $\langle R(T_h) \rangle$ of the upper (hot) side (corresponding to half of a TE parallelepiped) is given by

$$\langle R(T_h) \rangle = \int_{L/2}^L \frac{\rho(T_z)}{S} dz = \int_T^{T_h} \frac{\rho(T_z)}{S} \frac{dz}{dT_z} dT_z \quad (\text{A.4})$$

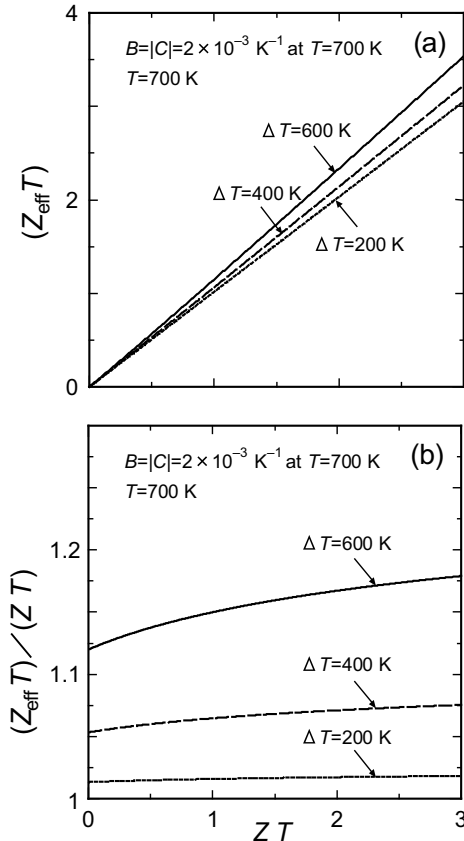


Fig. 6. (a) The effective $(Z_{\text{eff}} T)$ calculated at $T = 700$ K as a function of ZT using Eq. (30) by ascribing the increase in η due to $B = |C| = 2 \times 10^{-3} \text{ K}^{-1}$ to the increase in the intrinsic ZT and (b) the ratio $(Z_{\text{eff}} T)/(ZT)$ calculated as a function of ZT using Eq. (30).

Using the relation $dT_z/dz = \Delta T/L$, $\langle R(T_h) \rangle$ is obtained as

$$\langle R(T_h) \rangle = (R(T)/2)(1 + B\Delta T/4) \quad (\text{A.5})$$

In the same way, the average $R(T_c)$ is also derived as

$$\langle R(T_c) \rangle = (R(T)/2)(1 - B\Delta T/4) \quad (\text{A.6})$$

$\langle R(T_h) \rangle$ is higher by $BR(T)\Delta T/4$ than $\langle R(T_c) \rangle$ for $B > 0$.

Next, if the thermal conductivity κ changes linearly with temperature, $\kappa(T_z)$ at T_z is then expressed as

$$\kappa(T_z) = \kappa(T)[1 + (T_z - T)C], \quad (\text{A.7})$$

where

$$C = \frac{1}{\kappa(T)} \frac{d\kappa(T_z)}{dT_z} = \frac{1}{K(T)} \frac{dK(T_z)}{dT_z} \quad (\text{A.8})$$

When there is a temperature difference ΔT along a TE element, therefore, the resultant $\langle K(T) \rangle$ of a TE element is given by

$$\begin{aligned} \frac{1}{\langle K(T) \rangle} &= \frac{1}{S} \int_0^L \frac{1}{\kappa(T_z)} dz = \frac{1}{S} \int_{T_c}^{T_h} \frac{1}{\kappa(T_z)} \frac{dz}{dT_z} dT_z \\ &= \frac{1}{SK(T)\Delta TC} \ln |[1 + (C\Delta T)/2] / [1 - (C\Delta T)/2]|. \end{aligned} \quad (\text{A.9})$$

For $\Delta TC/2 \ll 1$, the resultant $\langle K(T) \rangle$ is expanded in a power series in ΔTC as

$$\langle K(T) \rangle = K(T)[1 - (C\Delta T)^2/12], \quad (\text{A.10})$$

where $K(T) = S\kappa(T)/L$.

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